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## 13. ABSTRACT (Maximum 200 words)

**Abstract:** Interfacial electron transfer (ET) in a prototypical semiconductor-liquid junction system (aq.  $\text{Fe}(\text{CN})_6^{4-}$  with  $\text{TiO}_2$ ) can be initiated by directly pumping a molecule to surface charge transfer transition ( $\lambda_{\text{max}} \approx 430\text{nm}$ ). The return electron transfer (ET) kinetics, which can be monitored by visible-region transient-absorbance spectroscopy, reveal a well-defined fast component ( $\tau = 270\text{ns}$ ) and a less well defined slow component ( $\mu\text{s} \rightarrow \text{ms}$ ). Detailed studies in the shorter time regime show that: 1) the interfacial ET rate is independent of laser pump power and, therefore, truly first order, 2) the kinetics are activationless, and 3) the kinetics are inverted, i.e. the ET rate decreases when the free energy driving force is increased by increasing the formal potential of the iron(III)-based electron acceptor. The results are broadly consistent with the predictions of contemporary, multimode quantum rate theories; they are also consistent with the findings of a prior study (by time-dependent scattering) of the Franck-Condon effects accompanying the reaction.

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**Technical Report No. 13**

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**Evidence for Inverted Region Kinetic Behavior**

**DTIC QUALITY INSPECTED 4**

**Hong Lu, Janice N. Preiskorn  
and Joseph T. Hupp**

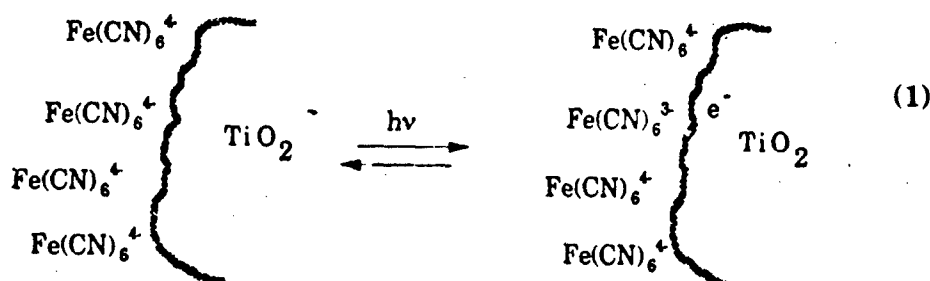
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Both classical<sup>1</sup> and quantum mechanical<sup>2,3</sup> theories of electron transfer (ET) lead to the now familiar - but nevertheless remarkable - prediction that ET rates should ultimately decrease with increasing thermodynamic driving force ( $-\Delta G^\circ$ ). While these predictions of "inverted" rate behavior remained controversial and largely unsupported for a number of years,<sup>4</sup> more recent studies have convincingly demonstrated their veracity for a range of organic,<sup>5</sup> inorganic/organometallic,<sup>6</sup> and biological<sup>7</sup> redox processes in both liquid and frozen homogeneous solution environments. To the best of our knowledge, however, the phenomenon has never been demonstrated for interfacial or electrochemical processes; indeed there are solid theoretical reasons to suspect that interfacial rate inversion would, in many cases, be impossible.<sup>1,8</sup> Nevertheless, we now report the first experimental demonstration of fast, inverted, interfacial ET rate behavior and show that it is broadly consistent with the predictions of the most sophisticated contemporary theories.<sup>2,3</sup>

The prototypical reaction examined was ET from colloidal  $\text{TiO}_2$  (a large bandgap semiconductor) to ferricyanide.<sup>9-11</sup> The reaction was initiated photochemically by pumping the tail of a *direct* (i.e. not dye sensitized) molecule-to-surface charge-transfer transition (eq.1;  $\lambda_{\text{max}} \approx 430\text{nm}$ )<sup>10,11</sup> with the amplified and doubled output of an Nd:YAG laser (532nm, 2.5ns pulses, 3 to 80mJ/pulse). Kinetics were monitored by following (at 488nm) the recovery of the charge-transfer absorbance.



For reaction 1, the recovery kinetics are characterized by a short ( $\tau = 270\text{ns}$ ) exponential decay and a much longer ( $\mu\text{s} \rightarrow \text{ms}$ ) nonexponential decay.<sup>12</sup> While both processes are evidently ET related we will further concern ourselves only with the better defined, shorter decay. This decay is responsible for roughly half of the total absorbance change.

Interpretation of the short decay in terms of interfacial ET kinetics yields  $k_{\text{ET}} = 3.7 \pm 0.4 \times 10^6 \text{s}^{-1}$ .<sup>13</sup> Variations in pump power (25-fold) confirm that the decay is truly first order, i.e. effectively a geminate interfacial charge-transfer process. Temperature variations over an admittedly narrow range ( $25^\circ$ ) show no detectable change in lifetime, implying an activationless ET process. This result is fully consistent with our prior observation, by time-dependent Raman scattering methods, that the Franck-Condon barrier to ET is dominated by very high frequency (ca.  $2000 \text{cm}^{-1}$ ) cyanide stretching modes.<sup>11</sup>

Variations in driving force were introduced by replacing one  $\text{CN}^-$  ligand with any of several substituted pyridines.<sup>14</sup> Absolute driving forces have yet to be determined,<sup>15</sup> however, relative  $\Delta G^\circ$ 's can be inferred from  $\text{Fe}(\text{CN})_5\text{L}^{3-/2-}$  potentials (Table I). Figure 1 clearly shows that  $\log k_{\text{ET}}$  decreases as the relative driving force increases. Control experiments show: 1) no change in  $k_{\text{ET}}$  with added (excess) pyridyl ligand, and 2) no absorbance transient from either the  $\text{TiO}_2$  colloid or the complexes separately.

Expressed as an effective electrochemical transfer coefficient (or Brönsted slope)<sup>16</sup> the  $\log k_{\text{ET}}/E$  plot in fig. 1 yields  $\alpha \approx -0.2$ . This result is quantitatively consistent with the predictions of a multimode quantum rate theory described by

Jortner and co-workers,<sup>2,a,b</sup> provided that: 1) ET is regarded as highly exothermic,<sup>15</sup> 2) displacements in high-frequency intraligand modes and, to a lesser extent, intermediate frequency metal-ligand and semiconductor lattice modes provide the necessary Franck-Condon overlaps,<sup>11</sup> 3) the displacements are more-or-less the same for each member of the redox series, and 4) all electrons are supplied at a single energy at or near the conduction band edge,<sup>17</sup> rather than over a range of energies corresponding to multiple mid-bandgap surface states.

We note that assumption 2 has already been experimentally validated<sup>11</sup> and that assumption 3 is at least qualitatively supported by existing studies of the  $\text{Fe(CN)}_5\text{L}^n$  series in homogeneous (bimolecular) redox processes.<sup>20</sup> If the absolute energetics of electron transfer (item 1) can be assessed, then more detailed confrontations with theory should be possible. Finally, we also hope to assess the effects of semiconductor electrode potential<sup>11b,18</sup> (by replacing colloidal  $\text{TiO}_2$  with a single, high-area surface<sup>19</sup>). This should enable us to test assumption 4 and perhaps also gain significant physical insight into the longer timescale absorbance decay phenomenon.

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2. See, for example: (a) Jortner, J. J.Chem.Phys. 1976, 64, 4860. (b) Ulstrup, J.; Jortner, J. J.Chem.Phys. 1975, 63, 4358. (c) Van Duyne, R.P.; Fischer, S.F. Chem.Phys. 1974, 5, 183.
3. For a brief and very clear explication of contemporary theories, see: Brunschwig, B.S.; Sutin, N. Comm.Inorg.Chem. 1987, 6, 209.
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7. See, for example: McLendon, G. Acc.Chem.Res. 1988, 21, 160.
8. Most importantly, at metal surfaces the inverted rate effect would be circumvented by the ability to deliver electrons from a continuum of levels below the Fermi level.



9. Colloidal  $\text{TiO}_2$  samples were prepared as described previously,<sup>10,11</sup> and utilized in solutions of  $\text{pH} \approx 2.5$ . Although this  $\text{pH}$  lies below the first  $\text{pK}_a$  of ferrocyanide, the complex appears to deprotonate upon binding to the semiconductor.<sup>11</sup>
10. (a) Vrachnou, E.; Vlachopoulos, N.; Grätzel, M. J.Chem.Soc.Chem.Comm. 1987, 868. (b) Vrachnou, E.; Grätzel, M.; McEvoy, A. J. J.Electroanal.Chem. 1989, 258, 193.
11. (a) Blackburn, R.L.; Johnson, C.S.; Hupp, J.T. J.Am.Chem.Soc. 1991, 113, 1160. (b) Doorn, S.K.; Blackburn, R.L.; Johnson, C.S.; Hupp, J.T. Electrochim.Acta 1991, 36, 1775.
12. Grätzel et al.<sup>10b</sup> have reported single exponential decay kinetics with a half life of ca. 3 $\mu\text{s}$ . Almost certainly their preliminary observation corresponds to the long timescale, nonexponential decay we observe.
13. Listed here and in Table I are uncertainties from multiple measurements on multiple samples prepared from a single colloid solution. Rate variations by as much as 50% were observed, however, for multiple samples from multiple colloid solutions.
14. (a) Toma, H.E.; Malin, J.M. Inorg.Chem. 1973, 12, 1039. (b) Felix, F.; Ludi, A. Inorg.Chem. 1978, 17, 1782.
15. From interfacial charge transfer absorption maxima and line shapes, absolute  $-\Delta G^\circ$  values would appear to fall in the 14,000 to 20,000  $\text{cm}^{-1}$  range. This is considerably greater than the energy differences between the conduction band edge ( $E_{\text{CB}}$ ) for  $\text{TiO}_2$  in contact with  $\text{pH} = 2.5$  solution and

the formal potentials for the cyano iron complexes. Reconciliation would require either a large negative shift in  $E_{CB}$  or large positive shifts in  $E_r$  following binding of the anionic metal complexes to the positively charged colloid surface. We note that precedents exist for both: (a) Wang, C.M.; Mallouk, T.E. J.Phys.Chem. 1990, 94, 4276. (b) DeSilvestro, J.; Pons, S.; Vrachnou, E.; Grätzel, M. J. Electroanal.Chem. 1988, 246, 411.

16. See, for example: (a) Albery, W.J. "Electrode Kinetics", Ch. 4, Clarendon Press, Oxford, 1975. (b) Weaver, M.J. In "Comprehensive Chemical Kinetics"; Vol. 27, Compton, R.G., Ed.; Elsevier, Amsterdam, 1988. (c) Ram, M.S.; Hupp, J.T. J.Phys.Chem. 1990, 94, 2378.
17. "Near" in this context would mean near enough to make the overall reaction driving force substantially greater than the total ET reorganization energy.
18. (a) Rothenberger, G.; Fitzmaurice, D.; Grätzel, M. J.Phys.Chem. 1992, 96, 5983. (b) O'Regan, B.; Grätzel, M.; Fitzmaurice, D. Chem.Phys.Lett. 1991, 183, 89. (c) O'Regan, B.; Moser, J.; Anderson, M.; Grätzel, M. J.Phys.Chem. 1990, 94, 8720.
19. (a) O'Regan, B.; Grätzel, M. Nature 1991, 353, 737. (b) Liska, P.; Augustynski, J.; Grätzel, M.J. J.Am.Chem.Soc. 1988, 110, 1216.
20. A linear free energy relationship (LFER) has been reported by Toma and Creutz (Inorg.Chem. 1977, 16, 545) for redox quenching of photoexcited  $Ru(bpy)_3^{2+}$  by  $Fe(CN)_5L^{n-}$  species. Although there are caveats (see Toma and Creutz), the LFER finding is broadly consistent with the idea of approximately fixed reorganizational energies (fixed vibrational displacements) for the  $Fe(CN)_5L^{n-}$  redox series.

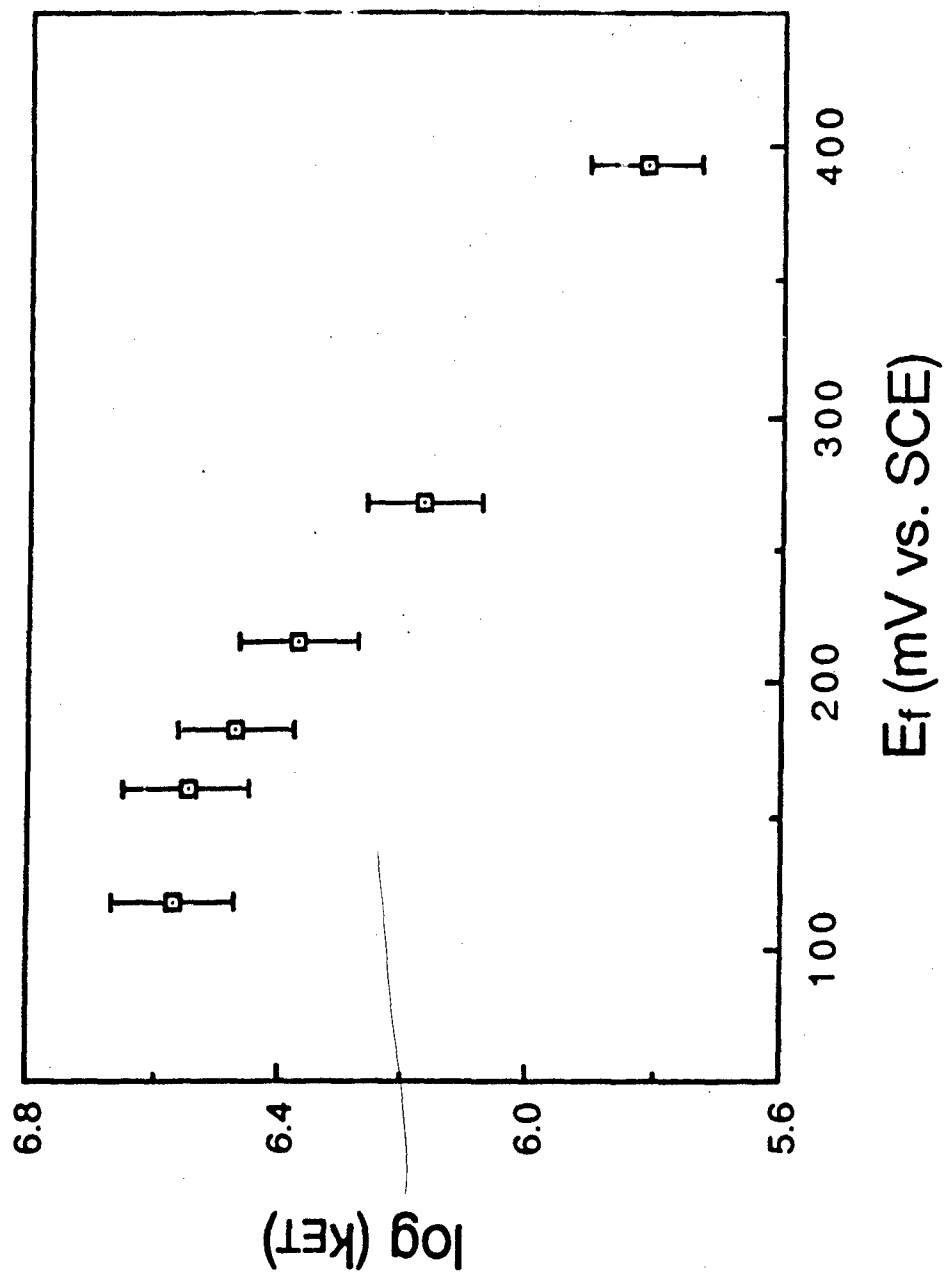
Table I. Solution Phase Formal Potentials and Interfacial Electron Transfer  
Reaction Times for  $\text{Fe}^{\text{III}}(\text{CN})_5\text{L}^-$  Species.

L	$E_f(\text{mV vs. SCE})^a$	$\tau(\text{ns})^b$
$\text{CN}^-$	$118 \pm 10$	$270 \pm 30$
3,5-dimethylpyridine	$160 \pm 20$	$280 \pm 30$
4-methylpyridine	$183 \pm 10$	$340 \pm 40$
pyridine	$215 \pm 10$	$430 \pm 40$
3-chloropyridine	$268 \pm 10$	$680 \pm 60$
pyrazine-ferrocyanide <sup>c</sup>	$393 \pm 10$	$1500 \pm 100$

a. Measured in 1M NaCl. b. Obtained at ca. pH 2.5. c. The reactant was  
 $(\text{NC})_5\text{Fe}^{\text{III}}\text{-pyrazine-Fe}^{\text{II}}(\text{CN})_5^{5-}$ .

Figure Caption

Log  $k_{ET}$  at colloidal  $TiO_2$  versus reduction potentials (solution phase) for  $Fe^{III}(CN)_5L^{n-}$  species.



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